

## Supporting Information

### Hollow/Rattle-type Mesoporous Nanostructures by A Structural Difference Based Selective Etching Strategy

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#### Experimental

##### Synthesis of Au@mSiO<sub>2</sub> nanorattles

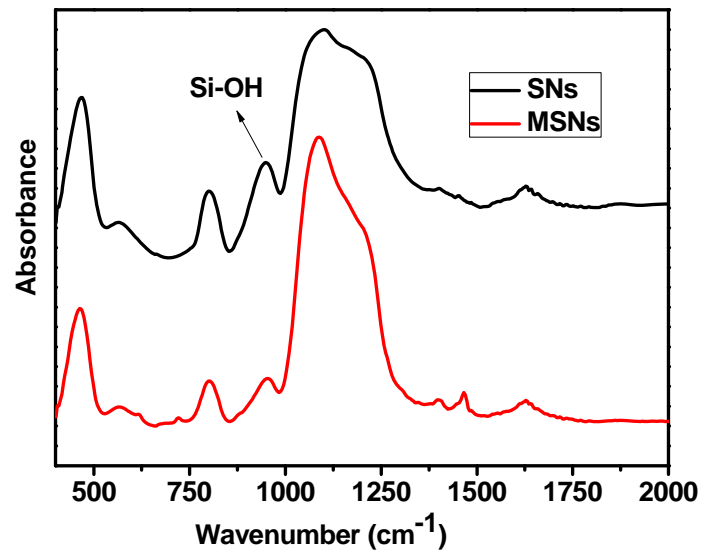
Au@SiO<sub>2</sub>@mSiO<sub>2</sub> were synthesized as follows. 18.0mg HAuCl<sub>4</sub>•3H<sub>2</sub>O was dissolved in 30mL water and heated to boil at 100°C under vigorous stirring. 1.0mL (3.0wt%) sodium citrate aqueous solution was injected quickly into above solution and then refluxed for 30 min. After the solution was cooled down to room temperature, an aqueous solution of PVP10 (polyvinylpyrrolidone, 12.8g/L, 0.235mL) was added to the colloidal gold solution to modify the surface of gold nanoparticles to facilitate silica coating. The solution was stirred for 24h at room temperature. The PVP-modified gold nanoparticles were collected by centrifugation and re-dispersed in 3.0mL water. 1.0mL PVP10 modified gold nanoparticles were added into a solution containing ammonia (0.62mL), ethanol (13.6mL) and water (3.3mL). After the ultrasonic treatment for 10min to disperse gold nanoparticles, a solution of TEOS (0.86mL) in ethanol (9.2mL) was injected under vigorous stirring. The reaction mixture was then stirred for another 1h. For mesoporous SiO<sub>2</sub> coating, a mixture of 0.714mL TEOS and 0.286mL C<sub>18</sub>TMS was injected under vigorous stirring and the reaction was continued for 1h. Au@SiO<sub>2</sub>@mSiO<sub>2</sub> were collected by centrifugation and dispersed in 0.05 M Na<sub>2</sub>CO<sub>3</sub> solution. The mixture was stirred vigorously at 80°C for 10 min. Then the products were centrifuged and washed with deionized water and ethanol several times. Finally, the products were dried at 100°C and calcined at 550°C for 6h.

## **Synthesis of rattle-type Fe<sub>2</sub>O<sub>3</sub>@mSiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub> ellipsoids**

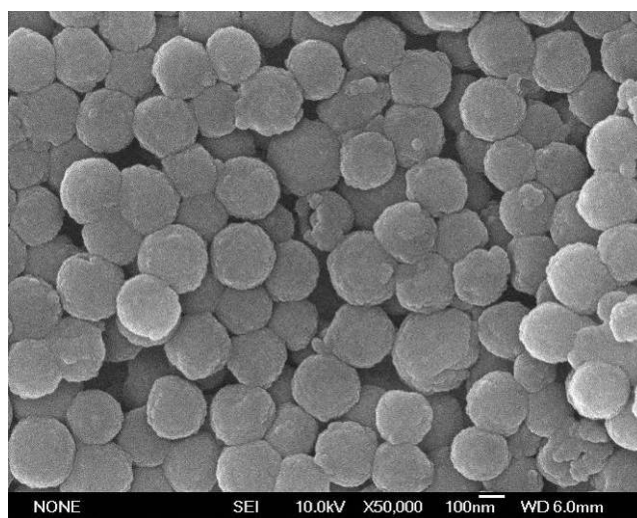
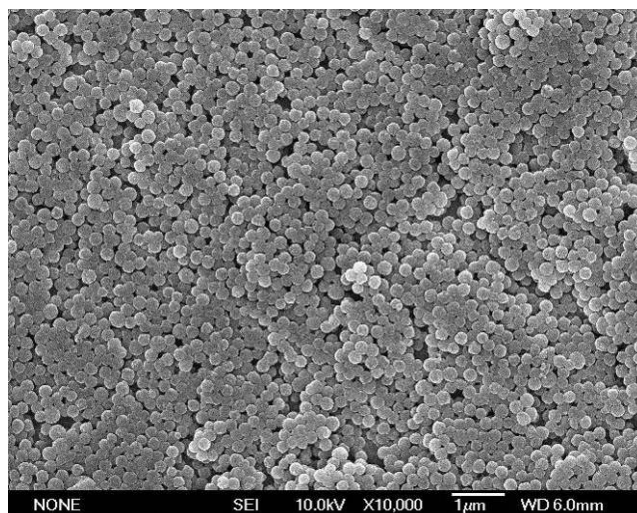
Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>@mSiO<sub>2</sub> sandwiched structures were synthesized as follows. Ellipsoidal Fe<sub>2</sub>O<sub>3</sub> were synthesized by aging a solution containing 11.6g Fe(ClO<sub>4</sub>)<sub>3</sub>•6H<sub>2</sub>O, 1.5g urea, and 0.16g NaH<sub>2</sub>PO<sub>4</sub> dissolved in 250mL deionized water at 100°C for 24h.<sup>14</sup> For SiO<sub>2</sub> coating, 30mg ellipsoidal Fe<sub>2</sub>O<sub>3</sub> were dispersed in a mixed solution of 71.4mL ethanol, 10mL H<sub>2</sub>O and 3.14mL ammonia solution. Then a mixture of 0.53mL TEOS and 4.7mL ethanol was added by an injecting pump at a speed of 4mL/h under vigorous stirring. For mesoporous SiO<sub>2</sub> coating, a mixture of 0.3mL TEOS and 0.2mL C<sub>18</sub>TMS was injected under vigorous stirring drop by drop. The resultant precipitate was collected by centrifugation for further use. For creating the cavities between Fe<sub>2</sub>O<sub>3</sub> and mesoporous shell to obtain rattle-type Fe<sub>2</sub>O<sub>3</sub>@mSiO<sub>2</sub> ellipsoids, the prepared Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>@mSiO<sub>2</sub> were treated in 0.12 M ammonia solution at 150 °C for 24h. Afterwards the products were centrifuged and washed with deionized water and ethanol several times. Finally, the products were dried at 100°C and calcined at 550 °C for 6h. To create the magnetic behavior of rattle-type composites, the reduction was carried out by the thermal treatment of Fe<sub>2</sub>O<sub>3</sub>@mSiO<sub>2</sub> in mixed H<sub>2</sub> (5% volume percentage) and Ar (95% volume percentage) gases at 410°C for 5h.

## **Synthesis of HMSs with large pores (11nm) in the shell**

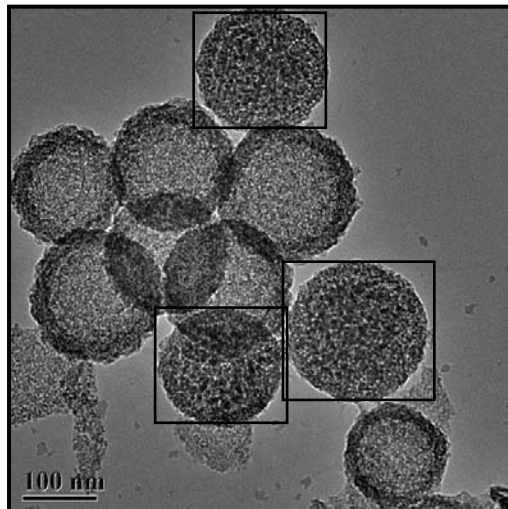
HMSs with large pores (11nm) were synthesized as follows: 6mL TEOS was added in the mixture of 71.4mL ethanol, 10mL deionized water and 3.14mL ammonia solution at 30°C. After the mixture was magnetically stirred for 1h, 5mL TEOS and 2mL C<sub>18</sub>TMS were then mixed and added into above mixture, which was magnetically stirred for another 1 hour. The product was centrifuged and dispersed in 0.6 M Na<sub>2</sub>CO<sub>3</sub> aqueous solution. The mixture was stirred for 4h at 80°C, followed by centrifugation and washing with deionized water several times. Afterwards, the products were dried at 100°C and calcined at 550°C for 6h.



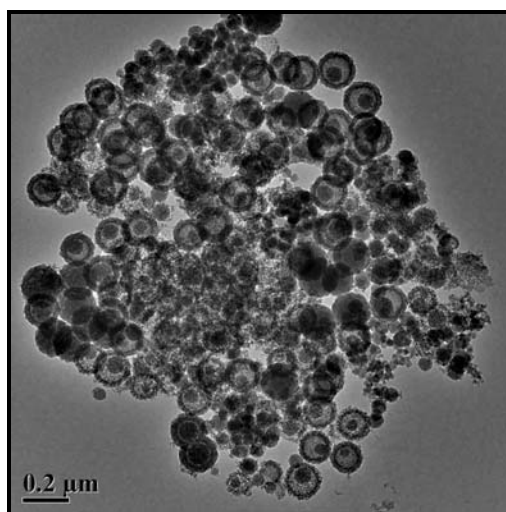
**Figure S1.** FTIR spectra of SNs and MSNs using absorbance as y-axis.



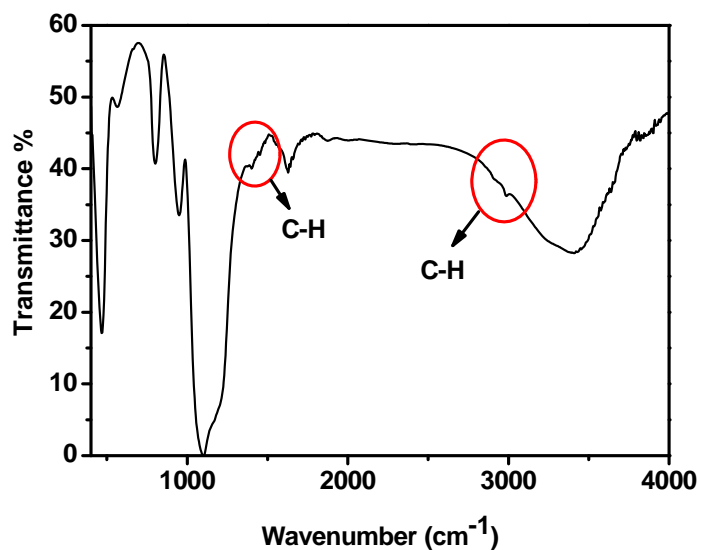
**Figure S2.** SEM images of homogeneous rattle-type mesoporous silica spheres achieved by treating  $s\text{SiO}_2@m\text{SiO}_2$  in 0.12 M ammonia solution at  $150^\circ\text{C}$  for 24h with different magnifications.



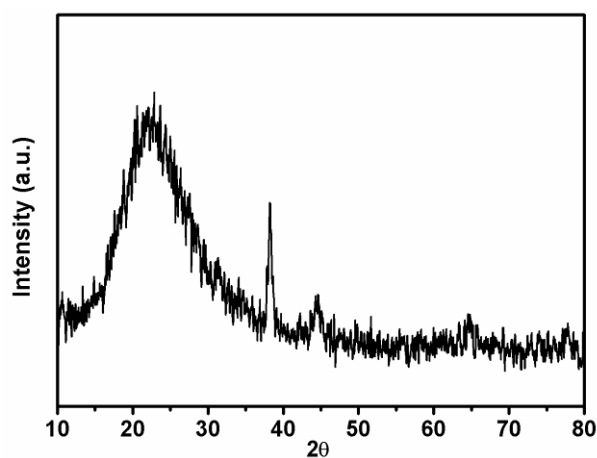
**Figure S3.** Hollow mesoporous silica spheres obtained by treating  $s\text{SiO}_2@m\text{SiO}_2$  in 0.2 M  $\text{Na}_2\text{CO}_3$  solution at  $80^\circ\text{C}$  for 0.5h.



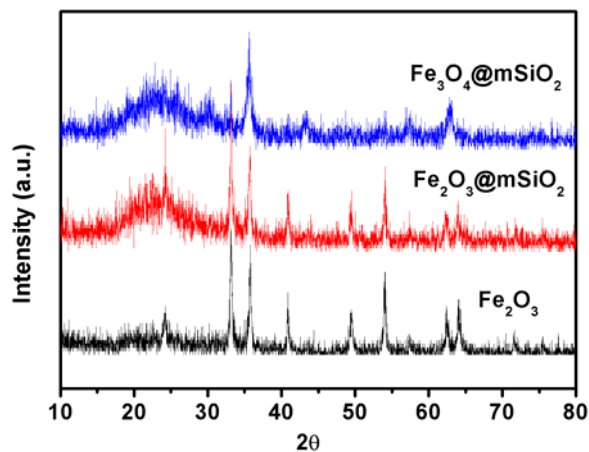
**Figure S4.** TEM images of hollow mesoporous silica spheres obtained by etching in 0.6 M  $\text{Na}_2\text{CO}_3$  solution for 0.5h after surfactant removal by calcination at  $550^\circ\text{C}$ .



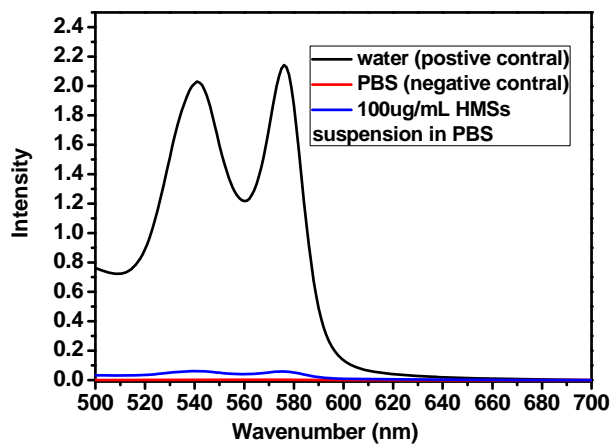
**Figure S5.** FTIR spectrum of SNs. The absorption bands between 1350 and 1500  $\text{cm}^{-1}$  and those between 2850 and 3000  $\text{cm}^{-1}$  could be attributed to the C-H bending and stretching vibrations of  $-\text{C}_2\text{H}_5$  groups, respectively, demonstrating the presence of  $\text{Si-O-C}_2\text{H}_5$  groups within SNs.



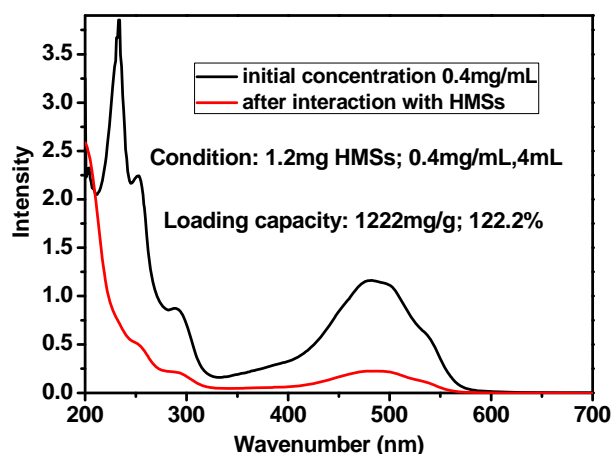
**Figure S6.** XRD pattern of rattle-type  $\text{Au@mSiO}_2$  by selective etching in  $\text{NaCO}_3$  aqueous solution.



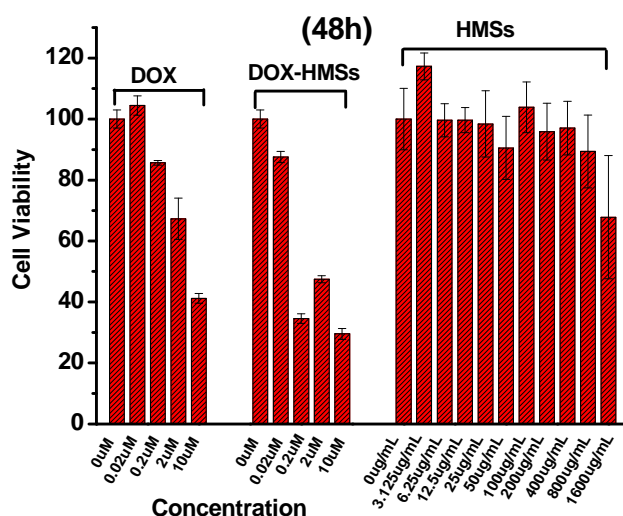
**Figure S7.** XRD patterns of ellipsoidal  $\text{Fe}_2\text{O}_3$  nanoparticles, rattle-type  $\text{Fe}_2\text{O}_3@m\text{SiO}_2$  by hydrothermal treatment in ammonia solution, and rattle-type  $\text{Fe}_3\text{O}_4@m\text{SiO}_2$  after final reduction in  $\text{H}_2$ .



**Figure S8.** UV-vis absorption spectra to detect the presence of hemoglobin at 541nm.

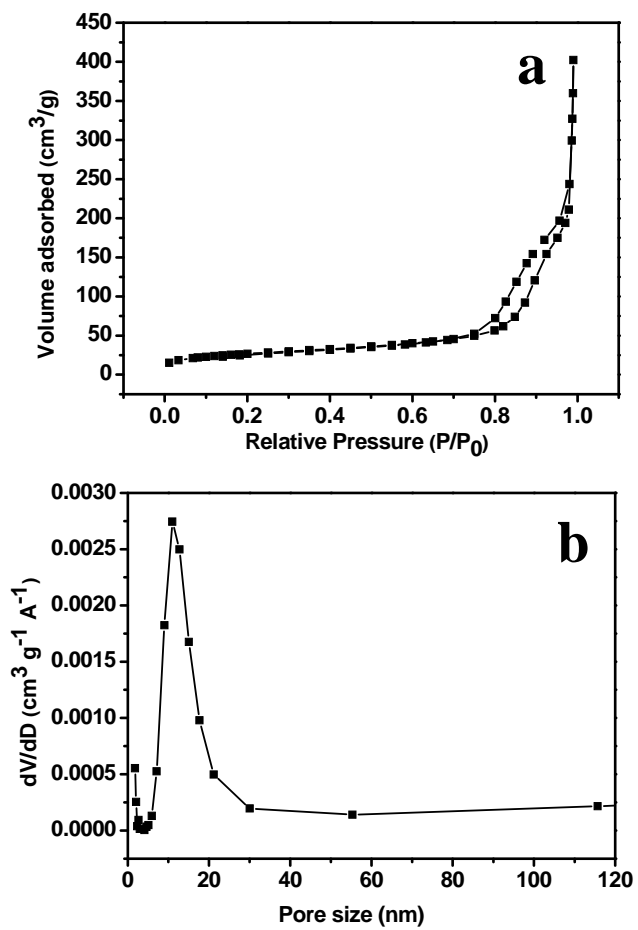


**Figure S9.** UV-vis absorbance spectra of DOX solutions before and after interaction with HMSs. To test the maximum loading capacity of HMSs, 1.2mg HMSs were immersed in 4mL 0.4mg/mL DOX PBS solution and stirred for 24h. The DOX loaded HMSs were obtained by centrifugation and the supernatant were obtained for UV-vis measurement. The calculated maximum loading capacity for DOX is 1222mg/g.



**Figure S10.** Cell viabilities of free DOX, DOX-loaded HMSs and HMSs at different concentrations in 48h.





**Figure S11.** N<sub>2</sub> adsorption-desorption isotherm of HMSs with the pore size of 11nm (a) and the corresponding pore size distribution (b).